VOLATILE ABUNDANCE OF PAIRED LUNAR TROCTOLITES AND THE EARLY LUNAR CRUST.

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Introduction: Nominally anhydrous minerals (NAMs) such as plagioclase, pyroxene, and olivine can contain small amounts of water and other volatile elements, typically within crystal lattice defects [1-5]. Given the volumetric abundance of NAMs, these minerals can contain a significant volatile reservoir despite their low abundances. At least one NAM is present in nearly all lunar rocks, unlike the more commonly studied volatile-bearing mineral apatite, making NAM-based hygrometry more widely applicable. NAMs are also not subject to enrichment in H due to self-fractionation of F, as is the case for apatite [6]. Recent developments in secondary ion mass spectrometry (SIMS) techniques (e.g., the reduction of analytical background) have allowed the evaluation of volatiles in samples that were previously too low in abundance to measure (e.g., [3,7,8]). The ability to make volatile measurements in the sub-10 ppm range opens up a suite of samples where volatile-bearing phases, such as melt inclusions and apatite, are rare or entirely absent. In this study we measure the abundances of H, C, F, P, S, and Cl in plagioclase from two paired lunar troctolites to better understand the volatile inventory of the early lunar crust and its implications for the bulk Moon.

Samples: The samples studied are Northwest Africa (NWA) 5744 and NWA 10140, which the Meteoritical Bulletin classifies as a granulitic troctolitic breccia and troctolitic anorthosite, respectively. These meteorites are believed to be paired with several other NWA meteorites. NWA 5744 is a recrystallized breccia composed mainly of plagioclase (up to 100 µm) with fine-grained (<50 µm) olivine, pigeonite, orthopyroxene, and accessory Ti-chromite and Ni-bearing troilite. NWA 10140 is a fine-grained anorthositic troctolite with plagioclase (75%), olivine (15%), and low-Ca pyroxene (10%) as dominant silicate phases. The thin-section for NWA 10140 was prepared specifically without the use of water. There are numerous shock melt domains present, some with quench spinifex textures. Accessory troilite and chromite were observed. The depths of origin for lunar troctolites is poorly understood, but in the peak-ring of the Schrödinger basin, olivine-bearing rocks that are potentially troctolites were uplifted from depths of 20 to 30 km [9].

Methods: Volatile abundances (reported as CO_2, H_2O, F, P_2O_5, S, and Cl) measurements were conducted using the Cameca ims 1280 ion-microprobe at the University of Hawai‘i at Mānoa. A Cs^+ primary beam of ~ 4nA was used, corresponding to a spot size of ~ 30 µm. The negative ions of interest were collected on the same spot using peak-jumping. To improve the analysis chamber vacuum and thus reduce the background contribution, a LN_2 cold trap and Ti sublimation pump were used. Background for water content was found to be 1.5 ppm H_2O with other elements significantly lower. Standards used are from [10] and [11]. Analyses were attempted on the minor olivine and pyroxene phases. Unfortunately, these grains proved to be too small and too pervasively fractured to provide robust data.

Results and Discussion: A total of 18 measurements forming several core-rim transects in six plagioclase grains were collected for NWA 5744 and 13 measurements from seven grains were collected for NWA 10140. Overall, the volatile contents of both meteorites are generally comparable to one another, as may be expected from paired samples. The C and H contents, however, are distinct. The C content of NWA 5744 plagioclase ranges from ~3 to 9 ppm CO_2, whilst values in NWA 10140 are lower and display a more restricted range (~0.8 to 2.2 ppm). The water (hydrogen reported as H_2O equivalent) content observed in NWA 5744 ranged from 0.4 to 1.0 ppm (average 0.6 ppm) whilst NWA 10140 contains ~ 1 ppm H_2O. The values from both samples are similar to those previously measured in lunar plagioclase from anorthosites and felsite clasts, which generally contained <10 ppm H_2O [2,3,5]. The fluorine content of both samples is generally less than 4 ppm (average 1.0 and 0.6 for NWA 5744 and NWA 10140, respectively); literature values for plagioclase have a greater range from below detection limits to ~45 ppm F [12,13]. Phosphorus (as P_2O_5) ranges from ~3 to 14 ppm in NWA 5744, whilst NWA 10140 displays a more restricted range (~3 to 6 ppm). Sulphur in both samples is at or below the detection limits for all analyses. The chlorine contents in both samples are very consistent, with both samples displaying Cl abundances of ~0.03 to 0.06 ppm.

Core-to-rim transects across the plagioclase grains are plotted in **Figure 1**. The Cl content in all transects appears to be low and invariant across the grain. No correlation is observed between F and H_2O for transect

a) or b), however, transect c) has a minor inverse correlation (R^2 = 0.65) (**Fig. 2**).

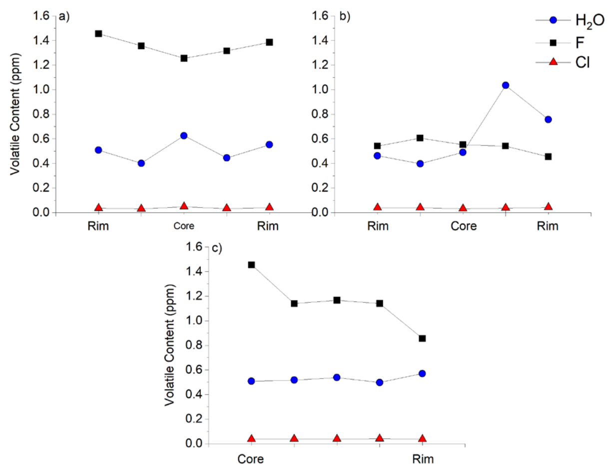

Figure 1: Volatile abundance data for three core-to-rim transects across plagioclase grains in NWA 5744.

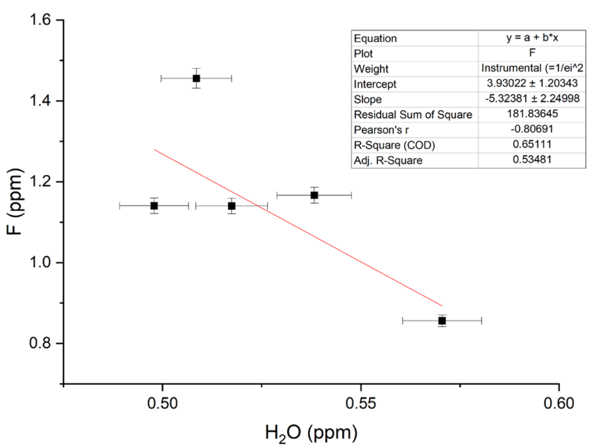

Figure 2: H_2O content vs. F content for one transect in NWA 5744 (transect c in Fig. 1).

The volatile content of a melt at the time of mineral crystallisation can be calculated using mineral-melt partitioning coefficients derived from measurements of minerals and glass in natural samples as well as determined experimentally (e.g., [4,14-16]). Natural terrestrial samples, however, formed under much higher pressures and oxygen fugacities than exist on the Moon, which affects the derived partition coefficients. To compound this, there are currently few experiments conducted under conditions relevant to the Moon [4,16]. This can lead to uncertainties in the calculation of melt volatile abundances. Therefore, to estimate the volatile composition of the melt, the partition coefficients for H_2O, F, and Cl based on available lunar experiments were used [16]. The average melt H_2O abundance calculated for NWA 5744 is 19 ppm, whilst NWA 10140 has an average of ~ 33 ppm. The lower of these estimates is similar to results found in [16] whilst the higher water estimate is above this range. Both, however, are below the ranges determined by [17] from lunar melt inclusions and values observed in [18]. Estimates for F and Cl are 12 ppm and 6 ppm, respectively for NWA 5744 and 8 ppm and 5 ppm for NWA 10140. The F estimates are slightly higher than previous lunar estimates [16,19,18], but lower than terrestrial halogen contents [20]. Chlorine estimates are significantly higher than previous lunar mantle estimates (~0.3 ppm [16,19,18]) but within the range estimated for terrestrial Cl (1.4 to 35 ppm Cl) [20].

Conclusions: This study provides a suite of volatile element abundances for two paired lunar troctolites. Generally, the water contents observed within samples is similar to previous literature values for lunar plagioclase, whilst fluorine is towards the low-end of the literature range. Estimates of the volatile melt composition for these samples suggest that water is similar to previous lunar mantle values but F and Cl are higher, with Cl within the range estimated for the primitive terrestrial mantle. The differences observed here further support the interpretation of a heterogeneous lunar mantle and provides further constraints on the early lunar crust.

References: [1] Peslier A. H. (2010) *J. Volcanol. Geotherm., 197*, 239–258. [2] Hui H. et al. (2013*) Nat. Geo., 6*, 177–180. [3] Hui H. et al. (2017) *EPSL, 473*, 14–23. [4] Lin Y. H. et al. (2019) *Geochem. Perspect. Lett., 10*, 14–19. [5] Simon J. I. (2020) *GCA, 276*, 299–326. [6] Boyce J. W. et al. (2014) *Science*, *344,* 400–402. [7] Peslier A. H. et al. (2019) *GCA*, *266,* 382–415. [8] Stephant A. et al. (2021) *GCA*, *297,* 203–219. [9] Kring D. A. et al. (2016) *Nature Comm.*, 7:13161, 10p. [10] Shimizu K. et al. (2017) *Geochem. J., 51*, 299–313. [11] Kumamoto K. M. et al. (2017) *Am. Min., 102*, 537–547. [12] Mosenfelder J. L. et al. (2017) *LPS XLVIII*, Abstract #2473. [13] Mosenfelder J. L. et al. (2019) *LPS L*, Abstract #2506. [14] Hamada M. et al. (2013*) EPSL, 365*, 253–262. [15] Warren J. M. and Hauri E. H. (2014) *J. Geophys. Res.*, *199,* 1851–1881. [16] Potts N. J. et al. (2021) *GCA*, *294,* 232–254. [17] Hauri E. H. et al. (2011) *Science, 333,* 213-215. [18] Hauri E. H. et al. (2015) *EPSL*, *409,* 252–264. [19] Ni P. et al. (2019) *GCA*, *249,* 17–41. [20] Klemme S. and Stalder R. (2018) in *The Role of Halogens in Terrestrial and Extraterrestrial Geochemical Processes*, 847–869.